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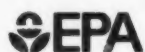
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Project Summary

Chemical Transformation Modules for Eulerian Acid Deposition Models: Volume I. The Gas-Phase Chemistry

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The study focuses on the review and evaluation of mechanistic and kinetic data for the gas-phase reactions that lead to the production of acidic substances in the environment. A master mechanism was designed that treats the chemistry of nitrogen oxides, sulfur dioxide, ozone, hydrogen peroxide, ammonia, the simple amines (methyl, dimethyl, trimethyl, and ethyl amines), chlorine, hydrogen sulfide, dimethyl sulfide, the hydrocarbons (methane, ethane, propane, butane, 2,3-dimethylbutane, the C_4 - C_6 alkanes, ethylene, propylene, trans-2-butene, isobutene, benzene, toluene, m-xylene, isoprene, alpha-pinene), and the variety of oxidation products of these species including the transient free radicals, aldehydes, ketones, hydroperoxides and other molecules. Reaction mechanisms and rate constants were identified for those chemical transformations for which major uncertainties remain and for which additional experimental and theoretical work is needed.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Early signs of ecological damage have been observed in certain sensitive areas of

the world that are deficient in soils with a good acid buffering capacity and that are recipients of a large input of acids through "acid rain" and/or dry deposition. Scientists throughout the world are actively working to assess the extent of damage that has occurred and can be expected to occur in years ahead. Government leaders of many nations are attempting to evaluate alternative control strategies for acid deposition that can alleviate the existing and potential future problems.

The understanding of the nature and importance of the various chemical pathways to acid generation within the troposphere is one of the several prerequisites to the development of scientifically sound strategy for the control of acid deposition. The present study was initiated as part of the research effort at the National Center for Atmospheric Research to develop a regional, Eulerian acid deposition model.

In most existing acid deposition models that have been employed in control strategy development, no attempt has been made to incorporate the many complex chemical processes that control acid generation. Existing models often involve the use of only fixed rates of transformation of SO_2 and NO_x to sulfuric acid and to nitric acid, respectively. Uncertainties in the source-receptor relationships that these models provide arise from many factors; among others, they are very sensitive to the rates of chemical transformation of the precursors to the acids. This sensitivity arises largely from the fact that the precursors of the acids and the acids

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themselves are not removed from the atmosphere with equal facility. Once sulfur dioxide is oxidized to sulfuric acid aerosol, it is dry deposited much less rapidly than is SO_2 . If aerosols composed of sulfuric acid and its salts (ammonium bisulfate, ammonium sulfate, etc.) are incorporated into precipitating clouds, then the deposition of these species can be faster than that of gaseous SO_2 . On the other hand, the nitric acid formed in the troposphere is much more rapidly deposited on the surface of the earth than are its precursors, NO and NO_2 . Thus, the amount of acid and the chemical nature of the acids deposited at sites many kilometers from the source of the precursors are sensitive functions of the rates with which the acids are formed as well as the rates with which these acids are transported by the motion of the air mass in which they are contained. It follows that the development of chemical modules for use in acid deposition models should be based upon chemical mechanisms that describe acid generation in terms of known rate laws and chemical theory.

In creating chemical mechanisms for modeling acid generation in the troposphere, there is no satisfactory analogue to the methods that were used to develop highly simplified, oxidant-generating mechanisms. These mechanisms depended heavily on the simulations of ozone generation in "smog chamber" experiments. The very products that are most important for models of acid development (sulfuric acid, nitric acid, hydrogen peroxide, etc.) are very short-lived in most chambers because of their removal at the walls of the chamber. No knowledge of their rates of generation or their concentrations in the free atmosphere can be derived from such experiments. Any reaction scheme, however, must eventually be tested or verified through simulation of actual rate data derived from both simple and complex reaction mixtures in the laboratory under conditions that simulate those of the troposphere or, preferably, in direct tropospheric measurements of the appropriate reactants and products. Although many aspects of the mechanism can be tested through use of laboratory and field data, verification of key aspects of the mechanism is not possible from the data available today.

In this work, a reasonably complete gas-phase mechanism has been formulated in an attempt to identify all of the potentially significant acid precursors and their chemistry. Simplification and

parameterization of the known chemistry can be made following suitable sensitivity tests on the complete chemical mechanism.

Approach

As a starting point in our evaluation, we compared the kinetic data (reaction mechanisms and rate constants) for over 200 reactions that have been used by various researchers to model the formation of photochemical smog. Based on these comparisons, we formulated a set of recommended rate constants for the reactions. Although the majority of the selected rate constants are in good accord with those recommended by others, there are some significant differences. Most of these differences are in the following areas: NO_x chemistry where recent extensive studies have been made; rate constants for the reactions of organic peroxy and alkoxy radicals; reactions of Criegee intermediates; and the photochemistry of the ketone, aldehyde, and other various oxidation products of the hydrocarbons. Some of the differences that exist in the hydrocarbon oxidation mechanisms result from differences in the interpretation of the existing, very limited data, including the effect of structure on the rate constants for the reactions of the peroxy and oxy radicals that result from the oxidation of the various hydrocarbons.

Based on mechanistic considerations, we formulated a more complete mechanism that is designated as the gas-phase "master mechanism" of acid generation. This mechanism includes the relevant inorganic chemistry involving NO , NO_2 , NO_3 , N_2O_5 , SO_2 , H_2S , O_3 , H_2O_2 , NH_3 , Cl_2 , HONO_2 , H_2SO_4 , HONO , HO_2NO_2 , CH_3SCH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, and $\text{C}_2\text{H}_5\text{NH}_2$. The tropospheric chemistry of several hydrocarbons is considered: methane, ethane, propane, n-butane, isobutane, 2,3-dimethylbutane, the $\text{C}_6\text{-C}_8$ alkanes, ethylene, propylene, trans-2-butene, isobutene, benzene, toluene, m-xylene, isoprene, and alpha-pinene. The chemistry of hydrocarbon oxidation products (aldehydes, ketones, peroxides, etc.) is also considered in some detail. The master mechanism includes the chemical reactions that lead to the development of the organic acids (formic acid, acetic acid, etc.). Although the master mechanism contains over one thousand elementary reactions, these reactions represent only a small fraction of the total tropospheric chemistry.

In the next stage of the planned effort, sensitivity studies will be made using the

master mechanism, and a simplified but scientifically realistic reaction scheme will be derived. Because of the immediate need for a working first-phase chemical transformation model, in separate parallel studies at NCAR, a highly simplified gas-phase and liquid-phase mechanism has been created using a more empirical approach that was less time consuming and consistent with the schedule for the phase-one model development. Suitable modification and replacement of elements of the preliminary mechanism will be made in accordance with the findings of this more detailed mechanism study.

After suitable simplification of the gas-phase chemistry mechanism has been achieved, the resulting reaction scheme will be coupled to a liquid-phase chemical mechanism. A sensitivity study of this mechanism is planned as well in order to develop the necessary simplified, combined gas-phase and liquid-phase chemistry module that is to be used in the final version of the Eulerian acid deposition model.

Results

A number of major uncertainties in the gas-phase chemistry mechanism was revealed during this study. Detailed sensitivity studies, however, will be required to determine which of these uncertainties induce significant changes in the rates of acid generation. Nevertheless, at this time it is possible to make a qualitative assessment of the master mechanism and to identify the key reactions for which present kinetic data are inadequate.

There are significant uncertainties that remain in the chemistry of the nitrogen compounds. N_2O_5 and NO_3 can be very important sources of nitric acid during the nighttime hours. Current literature shows a large divergence among the different experimental estimates of the equilibrium constant for the reaction, $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$. The calculated concentration of the reactive NO_3 radical and the significance of nitric acid formation are directly dependent on the value chosen for this equilibrium constant.

Several important mechanistic details that bear directly or indirectly on the generation of acids in the tropospheric oxidation of hydrocarbons, remain uncertain. In the case of alkanes, the major areas that require further study are: (a) the extent of nitrate formation from the reaction of peroxy alkyl radicals with nitric oxide, and (b) the relative rates of alkoxy radical decomposition, rearrangement, and disproportionation. Knowledge of the

mechanisms of tropospheric oxidation of alkenes is incomplete as well. The areas of greatest uncertainty include: (a) the rates of the beta-hydroxy-alkoxy radical decomposition and reaction with oxygen, and (b) the rate constants for the reactions of the Criegee intermediates with NO , NO_2 , H_2O , and SO_2 . The least well understood of the hydrocarbon oxidation mechanisms is that for the aromatic hydrocarbons. The present chemistry is not well established experimentally and requires further study before confidence can be placed in the mechanism and the influence of these species on HO , HO_2 , and RO_2 radical concentrations and acid production. Product mass balances are also poor for the oxidation of the natural hydrocarbons. Further elucidation of the chemistry of these systems will be necessary to determine the influence of these species on acid generation in the troposphere.

One of the most neglected areas of research is the chemistry of the carbonyl compounds. Photochemical quantum yield data for tropospheric conditions are not now available for most of the carbonyl species that form in the atmosphere. Experimental estimates of both the quantum efficiencies and the nature of the primary processes that generate free radicals are needed. It is also important to establish the extent of radical generation from aldehydes and ketones. These products are expected to have a significant influence on the chemistry that produces oxidants such as ozone and hydrogen peroxide.

Organic hydroperoxides can oxidize bisulfite ion readily to form sulfuric acid in cloud water. For tropospheric conditions, the most likely sources of these compounds are the reaction between HO_2 radicals and peroxy organic radicals. Only two of the many hundreds of these reactions that can occur in the troposphere have been studied kinetically. The gas-phase chemistry of the hydroperoxides is equally poorly defined. Quantitative information on both the photochemical processes and the reactions of HO radicals with the hydroperoxides are required.

The simplest of the peroxyacylnitrates has been shown to be a good oxidant of bisulfite ion in water solutions, and the higher homologues are probably effective as well. In addition, the decomposition of these compounds to form acylperoxy radicals and nitrogen dioxide can act as a source of nighttime acid generation. Rate data related to only two of the many peroxyacylnitrates now exist. Further

studies are needed to determine the role of these species in acid generation.

There are very few experimental data that allow an adequate test of the complex gas-phase mechanisms proposed to explain acid generation in the troposphere. The compounds that are most important in any evaluation (sulfuric acid, nitric acid, hydrogen peroxide, organic peroxides, hydrocarbons and their oxidation products) are usually not simultaneously measured in simulated atmospheric studies or in field studies. Such data are critical to any meaningful test of a mechanism. New experimental measurements of the important acids and acid precursors are required in both simulated and actual tropospheric air masses in order to test current chemistry mechanisms. The development of imaginative new methods for laboratory studies (other than typical smog chamber studies) is encouraged to minimize the wall removal of acids and acid precursors. Furthermore, it is recommended that field studies include measurements of reactive hydrocarbons, aldehydes, ketones, organic acids, hydrogen peroxide, methyl hydroperoxide, as well as the commonly measured compounds, NO_x , SO_2 , O_3 , H_2SO_4 , HNO_3 , and the salts of these acids. Vertical profiles of the concentrations should also be made at a variety of

locations in the eastern United States. Without such measurements, acid deposition models have an undesirable flexibility in the choice of initial reactant concentrations, and it is impossible to judge the accuracy of a mechanism from the limited experimental data.

Conclusions

In this study we formulated a reasonably complete set of gas-phase reactions in an attempt to identify all of the potentially significant acid-forming processes. The chemistry module that is to be used in our acid deposition model must be highly simplified in order to conserve computer time and allow efficient operation of the model. Because of this, considerable simplification of the reaction scheme presented in this study will be needed before it is suitable for use in our acid deposition model. In conducting this simplification, however, we do not want to sacrifice the ability of the model to predict the rates of acid generation with reasonable accuracy. We have concluded that the only way one can test adequately the scientific accuracy of any highly abbreviated chemical reaction scheme is to start from a scientifically sound reaction scheme that includes all relevant acid-forming chemical processes. This is the approach that was adopted in our study.

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Marcia C. Dodge is the EPA Project Officer (see below).

The complete report, entitled "Chemical Transformation Modules for Eulerian Acid Deposition Models: Volume I. The Gas Phase Chemistry," (Order No. PB 85-173 714 AS; Cost: \$22.00, subject to change) will be available only from:

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